40 atmospheres, but for higher pressures the product decreases as the gas approaches the liquid state.

The mean values for the products of the mobility and pressure in atmospheres, for the range of pressures for which the product was constant, are, for the negative and positive ions respectively, in dry air, 1·89 and 1·346; in dry hydrogen 8·19 and 6·20, and moist carbon dioxide 0·67 and 0·705 cm. per second for a potential gradient of 1 volt per centimetre.

In conclusion, I take great pleasure in expressing my best thanks to Prof. Rutherford for suggesting this research, and for the valuable advice given by him during the progress of the experiments.

On the Viscosities of Gaseous Chlorine and Bromine.

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(Communicated by Prof. F. T. Trouton, F.R.S. Received November 22, 1911,—Read January 25, 1912.)

Introduction.

The object of the experiments about to be described was to determine the viscosities, at various temperatures, of gaseous chlorine, bromine, and iodine, by comparison with air. The apparatus, however, proved unsuitable in several respects for working at the higher temperatures required. It has, nevertheless, yielded satisfactory results at the lower temperatures; and the viscosity of chlorine at atmospheric temperature and at 100° C., and that of bromine at the latter temperature only, have been measured by means of it. These values are now published, pending the extension of the investigation on the lines indicated, with a new form of apparatus which promises to be entirely adequate for the purpose.

The chief difficulty which presents itself in working with the halogen gases is the readiness with which they attack mercury. On this account, the method I have previously used* for viscosity determinations was rendered unsuitable; but it has been found possible to retain one of its most desirable features, viz., the mercury pellet, which serves the double purpose of creating a constant pressure difference, and of measuring the volume of

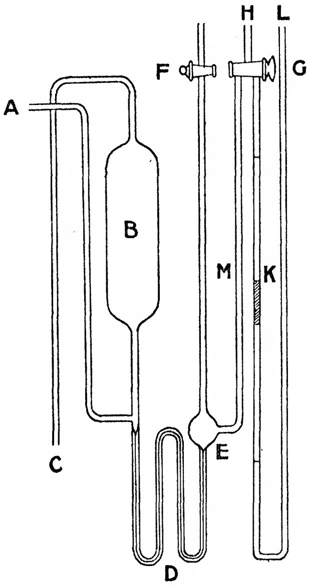
* 'Roy. Soc. Proc.,' A, vol. 83, pp. 265 and 516.

gas emerging from the capillary. In other respects the apparatus is quite different, the main object in its construction being to prevent contamination of the mercury. This has been sufficiently secured by causing the pellet to aspirate the gas through the capillary tube, with a deep layer of air acting as a kind of buffer between them. The failure of the method at high temperatures was chiefly due to the mercury pellet becoming unstable, owing to the diminution of surface tension.

Apparatus and Experimental Method.

The principle of the method will be gathered from fig. 1, which represents the apparatus in semi-diagrammatic form. Only the essential features are shown. B is a bulb of about 100 c.c. capacity, which could be filled with the gas under test. The capillary tube D consists of rather more than a metre of fine-bore tubing, the internal diameter of which is about 0·2 mm. This is bent, as shown, in order to save space, and the exit leads into a small bulb E, which is of sufficient capacity to contain easily the gas drawn through the capillary during one determination. The tube in which the mercury pellet moves is marked K in the diagram. By means of the tap G it may be connected with E through the tube M; and, under these circumstances, the pellet creates a constant pressure difference between the two ends of the capillary; for the end L is open to the atmosphere, as also is C. The volume of gas sucked through the capillary is indicated by the distance moved through by the pellet. Thus we may obtain an approximate measure of the ratio of the viscosities of two gases by comparing the times of fall of the mercury pellet between two fixed marks on the tube K, when the two gases, in turn, occupy the bulb B and the tubes leading to it. In the present apparatus the bore of the tube K is about 3 mm. in diameter, the length of the pellet about 9 cm., and the volume of gas drawn through the capillary in one determination is about 4 c.c. This gas, on emerging, occupies the bulb E, and, except by diffusion through the long tube M, does not reach the mercury pellet. By this means it is possible to avoid contamination of the mercury, or, at any rate, to delay it sufficiently for a series of consistent measurements to be made.

Figure I.



In order to repeat the experiment two things are necessary: the mercury pellet must be raised, and the gas in E must be replaced by air. These are done in the following way:—The end H is connected to a large reservoir of air, the pressure of which is kept below that of the atmosphere by an amount slightly exceeding the pressure arising from the mercury pellet. The tap G can be used to connect the tube K with H, and the pellet is then sucked to the top of the tube. Connection between M and H can also be secured by means of G, and then by opening the tap F dry air may be drawn through E so as to displace the gas it contains. The tap F is then closed, but before connecting M and K, M is connected with H in order to avoid the large immediate fall of the mercury pellet which would otherwise take place, owing to the expansion of the air in E and M.

It was at first expected that the great density of chlorine and bromine might be relied on to prevent considerable mixture through convection and diffusion of air into B through C, which, as before stated, was open to the atmosphere. This, indeed, turns out to be the case with bromine. But preliminary experiments with carbon dioxide showed that it would be better to allow the gas to overflow slowly throughout the series of measurements, and this has therefore been done.

Further, the exit C was arranged at the same level as E, so as to practically eliminate the small hydrostatic pressure arising from the gas itself. The pressure difference was therefore in all cases the same, viz., that determined by the mercury pellet. The whole apparatus, with the exception of the tubes A, C, and L, and the taps G and F, was immersed in suitable baths, first in a water reservoir at atmospheric temperature, and afterwards in a double-walled steam jacket.

In each case the viscosity has been compared with that of air under exactly similar conditions, the values obtained being

$$\eta_{\mathrm{Cl}}/\eta_{\mathrm{air}} \text{ at } 12{\cdot}7^\circ \text{ C.,} \quad \eta_{\mathrm{Cl}}/\eta_{\mathrm{air}} \text{ at } 99{\cdot}1^\circ \text{ C., and } \eta_{\mathrm{Br}}/\eta_{\mathrm{air}} \text{ at } 98{\cdot}7^\circ \text{ C.}$$

The chlorine was prepared by the addition of pure hydrochloric acid to potassium permanganate, the gas then being washed, dried, and condensed in a bulb immersed in alcohol cooled by solid carbon dioxide. It was then allowed to evaporate slowly and entered the apparatus by way of a glass spiral which was kept at the temperature required for the particular experiment. This secured that the gas used had the proper temperature.

The bromine used was of the purest quality obtainable from Kahlbaum. It was mixed with phosphorus anhydride and thence distilled directly into the apparatus. The gas under these circumstances entered at the temperature of boiling bromine (about 60° C.), and did not attain the required temperature (100° C.) so long as the flow continued. Hence the observed times of fall of the mercury pellet during this stage were lower than those obtained after evaporation had ceased, when the gas really assumed the temperature of the bath. A considerable number of minutes elapsed before a further and progressive increase in the times of fall ensued, owing to the slow diffusion of air into the bulb B. The values used in the determination were therefore those following the complete evaporation of the bromine and previous to the increase due to diffusion of the air.

Results.

The following determination is given in detail to illustrate the probable accuracy of the method and the mode of treatment of the observations.

September 27, 1911. Barometer, 76·50 cm. Temperature, 99·1° C.

	Times of fall in seconds.	
	Air.	Chlorine.
	200·2	155·6
	199·8	154·6
	199·6	154·6
	200·2	154·6
	199·6	154·2
	199·4	155·0
		154·4
Mean	199·8	154·7

The approximate value of the ratio $\eta_{\text{Cl}}/\eta_{\text{air}}$ at 99·1° C. is therefore 154·7/199·8 = 0·7743. This has to be corrected for the difference of slipping coefficients of chlorine and air. The method of doing this has been previously described,* and need not be repeated here. The corrected value is

$$(\eta_{\text{Cl}}/\eta_{\text{air}})_{99\cdot1} = 0\cdot772.$$

The value of η_{air} at 99·1° C. found by the author† is $2\cdot186 \times 10^{-4}$ C.G.S.

Hence at 99·1° C. $\eta_{\text{Cl}} = 1\cdot688 \times 10^{-4}$ C.G.S.

The other value for chlorine obtained is that at 12·7° C. At this temperature

$$(\eta_{\text{Cl}}/\eta_{\text{air}})_{12\cdot7} = 0\cdot726.$$

At 12·7° C. $\eta_{\text{air}} = 1\cdot786 \times 10^{-4}$ C.G.S. Hence

$$\eta_{\text{Cl}} = 1\cdot297 \times 10^{-4} \text{ C.G.S.}$$

In the case of bromine

$$(\eta_{\text{Br}}/\eta_{\text{air}})_{98\cdot7} = 0\cdot8557.$$

At 98·7° C. $\eta_{\text{air}} = 2\cdot184 \times 10^{-4}$ C.G.S.

Hence $\eta_{\text{Br}} = 1\cdot869 \times 10^{-4}$ „

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* 'Roy. Soc. Proc.,' A, vol. 83, pp. 517 and 518.

† 'Roy. Soc. Proc.,' A, vol. 84, p. 191.

The collected values are given below:—

Gas.	Temperature.	$\eta \times 10^4$ C.G.S.
Chlorine	12·7° C.	1·297
Chlorine	99·1°	1·688
Bromine.................	98·7°	1·869

Assuming that Sutherland's law holds for chlorine over this temperature range, we may calculate the value of the constant C in the equation

$$\eta = K \frac{T^{\frac{1}{2}}}{1+C/T},$$

which may be put in the more convenient form

$$\frac{\eta_2}{\eta_1} = \left(\frac{T_2}{T_1}\right)^{\frac{3}{2}} \left(\frac{C+T_1}{C+T_2}\right).$$

From the values given above,

$$\eta_{99\cdot1}/\eta_{12\cdot7} = 1{\cdot}302,$$

and the value thus obtained for C is 325.

It should be pointed out, however, that this may have a very considerable error, owing to its sensitiveness to variation in the ratio $\eta_{99\cdot1}/\eta_{12\cdot7}$. If we suppose that this ratio is subject to an error of $\frac{1}{2}$ per cent. (and this represents approximately the order of accuracy of the measurements), C will have a value lying between 305 and 352. Thus the value given may be 9 per cent. from the true value, and a more reliable estimate cannot be made until the measurements are extended to higher temperatures.

Discussion of Results.

It is interesting to observe the bearing of these results upon the two laws with reference to viscosity to which the author has previously called attention. These may be stated as follows:—

(i) For most of the gases for which data are available Sutherland's constant is proportional to the critical temperature, or

$$T_c/C = \text{constant} = 1{\cdot}14.$$

(ii) For the group of inert gases the square of the viscosity at the critical temperature is proportional to the atomic weight, or

$$\eta_c^2/A = \text{constant} = 3{\cdot}93 \times 10^{-10}.$$

The first of these laws may be tested with respect to chlorine. The critical temperature of this gas is in the neighbourhood of 416° absolute. For chlorine, therefore,

$$T_c/C = 416/325 = 1{\cdot}28,$$

a number which is considerably in excess of the value for other gases. It should be noticed, however, that the possible error in C referred to above is quite sufficient to account for the divergence.

The second law cannot be tested directly, for the variation with temperature of the viscosity of bromine is not known. If, however, we calculate the viscosities of chlorine and bromine at *corresponding* temperatures, *i.e.* temperatures which bear equal ratios to the respective critical temperatures, we find that a similar rule applies in this case also.

The critical temperature of bromine is 575° absolute. The temperature at which the viscosity of bromine is known is 371·7° absolute, or 0·6466 of the critical temperature. The corresponding temperature for chlorine is $416 \times 0{\cdot}6466 = 269°$ absolute. The viscosity of chlorine at this temperature may be found by extrapolating over the small range of 17° C., since the viscosity at 12·7° C. or 285·7° absolute is known. The results are as follows:—

Temperature $= 0{\cdot}6466\ T_c$.

Gas.	$\eta \times 10^4$.	A.	η^2/A.
Chlorine	1·218	35·5	$4{\cdot}19 \times 10^{-10}$
Bromine	1·869	80·0	$4{\cdot}37 \times 10^{-10}$

The two numbers in the last column differ by only 4 per cent., notwithstanding the fact that any error in η has been doubled by the process of squaring. This constancy at least suggests that for the halogen group of gases η_c^2/A is probably also constant, although not the same constant as for the inert gases. Indeed, it may be shown that if for a group of gases the two laws referred to above hold, it follows that at all corresponding temperatures η^2/A is constant.

Let θ denote the ratio T/T_c. Then Sutherland's formula assumes the form

$$\frac{\eta}{\eta_c} = \theta^{\frac{3}{2}} \left\{ \frac{C/T_c + 1}{C/T_c + \theta} \right\}.$$

Now, if $C/T_c = \text{constant}$ (as is the case for the majority of gases), it follows that for equal values of θ

$$\eta/\eta_c = \text{constant}.$$

Hence, if η_c^2/A is constant, η^2/A at corresponding temperatures is necessarily also constant. The latter rule has been shown to hold in the case of chlorine and bromine at one pair of corresponding temperatures only, and although this does not prove that a similar rule holds at the critical temperatures, the probability is that the extension of the investigation will show this to be the case.

On the Relation between Current, Voltage, Pressure, and the Length of the Dark Space in Different Gases.

By F. W. Aston, B.Sc., Trinity College, Cambridge, and H. E. Watson, B.Sc., 1851 Exhibition Scholar, Trinity College, Cambridge.

(Communicated by Sir J. J. Thomson, F.R.S. Received December 7, 1911,—Read January 25, 1912.)

In a previous communication by one of us* the results of a number of experiments on the relation between current, voltage, pressure, and the length of the dark space were given for the gases hydrogen, nitrogen, oxygen, and air. The first part of the present paper consists of a continuation of that communication giving the results obtained with carbon monoxide, argon, and helium, together with some constants for these and the gases previously mentioned which were not published at the time.

The second part deals with a systematic investigation of the behaviour of the inactive gases when in a state of great purity.

Part I.—For detailed description of the apparatus and method employed the reader is referred to the above-mentioned paper. It will be sufficient to state here that the discharge took place between aluminium discs, 10 cm. in diameter and about 17 cm. apart, the cathode being of the guard-ring type to ensure accurate measurements of the current density.

The case of *carbon monoxide* is particularly interesting as it is the only compound gas yet experimented on which allows the passage of a continuous current without very serious decomposition. In its behaviour it resembles exactly the active elementary gases. Its dark space is sharp and well defined, but if the current density is increased beyond a certain limit (about half the maximum used for the other gases), the discharge strikes back behind the cathode, and consequently the values of constants obtained are not very accurate.

The *argon* used was certainly impure, for it showed no signs of the primary

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* F. W. A., 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 80.